Metal-based non-aqueous redox flow batteries with highly soluble active species and improved performance

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The global energy economy currently experiences a shift towards renewable energy resources, which comes along with fluctuations in power output, depending on factors such as weather and season. Energy storage is a key technique which ensures the smooth and consistent power output of renewable energy resources. Redox flow batteries (RFBs) have become one of the most promising candidates for such large scale energy storage due to their flexible design, high efficiency and long cycle life. Compared with widely studied aqueous RFBs, non-aqueous RFBs allow for higher cell voltages and energy densities [1-5]. Besides, it is possible to operate non-aqueous RFBs at temperatures below the freezing point of the electrolyte of aqueous RFBs. Therefore, the research on the non-aqueous RFBs (e g. metal-based and all-organic RFBs) is developing rapidly.

In this study, metal-containing ionic liquids with bis(trifluoromethylsulfonyl)imide (Tf_2N) anions were proposed as active species for non-aqueous RFBs. Tetrakis(acetonitrile)copper(I) bis(trifluoromethylsulfonyl)imide($[Cu(MeCN)_4][Tf_2N]$) showed a very high solubility of 1.68 M in acetonitrile, the most widely used organic solvent for non-aqueous electrochemical applications. Hence, a maximum theoretical energy density around 28 Wh L^{-1} can be reached with the reported system. The Cu^{2+}/Cu^{+} and Cu^{+}/Cu couples in this system yield a cell potential of 1.24 V. The diffusion coefficient for $[Cu(MeCN)_4][Tf_2N]$ in acetonitrile is estimated by rotating disk electrode experiments to be 6.8×10^{-6} cm^2 s^{-1}. The RFB with this electrolyte shows a promising performance, with coulombic efficiencies of 87 % and energy efficiencies of 44 % at current density of 5 mA cm^{-2}.

Supporting electrolytes were investigated to increase the conductivity of the electrolytes. Four types of ionic liquids with Tf_2N anions and different cations (tetraethylammonium, choline, trioctylmethylammonium and 1-butyl-3-methylimidazolium, respectively) were evaluated by cyclic voltammetry experiments and conductivity measurement.

Solvent-resistant anion exchange membranes(AEMs) were prepared to improve the battery performance and study the Tf_2N anions transport properties over the AEMs. The AEM based on poly(phenylene oxide) (PPO) polymer was prepared by cross-linking to obtain the quaternary ammonium groups without involvement of harmful trimethylamine. A semi-interpenetrating network structure was thus constructed inside the membrane, hence ensuring both ion transport and solvent resistance. The ion exchange capacity (IEC) of membrane was tuned by the crosslink agent content, and the membrane showed a good anion conductivity and retention of copper ions. The RFB single cell with this crosslinked membrane yielded a coulombic efficiency of 89 %, a voltage efficiency of 61 % and an energy efficiency of 54 % at 7.5 mA cm^{-2}. This provides a simple and effective way to develop suitable AEMs for non-aqueous RFB applications.

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